

## \* NOTICES \*

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the method for film deposition of the vacuum treatment chamber having an evaporation source and an evaporation source, and an organic compound film. More particularly, for example The insulator layer of a semiconductor device, a passivation film, a soft error film, When forming the organic compound film used for the dielectric of liquid crystal orientation and a plastic capacitor, the heat insulation film of an injection molding die, etc., it is related with the method for film deposition of the vacuum treatment chamber having the evaporation source and evaporation source which are used in order to evaporate the raw material monomer of this organic compound film, and an organic compound film.

[0002]

[Description of the Prior Art]Conventionally, the organic compound used as the raw material monomer of said organic compound film has high steam pressure compared with an inorganic compound, it evaporates in the degree of low temperature (sublimation), and, generally the evaporating temperature in the inside of a vacuum is in the range of minus 10\*\* to plus 250 \*\*.

[0003]And as an evaporation source which evaporates the raw material monomer of this kind of organic compound film, What carries out direct heating of the raw material monomer, and evaporates it by resistance heating using a boat conventionally, what carries out radiation heating and evaporates a raw material monomer with radiation devices, such as a heating heater allocated near the boat, -- or, The thing etc. which make the gaseous raw material monomer produced by carrying out heating evaporation on the outside of the vacuum treatment chamber like the usual CVD (Chemical Vapor Deposition) method introduce in a vacuum treatment chamber via piping are known.

[0004]

[Problem(s) to be Solved by the Invention]The commercial organic compound is used for the raw material monomer of the conventional organic compound film as it is. However, in a ready-made article, since purity is not 100%, the actual condition is that at least 0.1% or more of impurity is included. For example, supposing the value of standard of the factory shipments in the case of pyromellitic dianhydride is 99.2% of purity, in 1 kg, at least 8-g impurity will already be included. It reacts to the water (humidity) in the atmosphere, etc. depending on the kind of raw material monomer, and a storage situation, and also an impurity is made increased.

[0005]It will remain as particle and a film with unevenness or a pinhole will be made without these impurities reacting into a film, if the vapor-deposition-polymerization film of an organic compound is formed on a substrate using the raw material monomer of these organic compound film.

[0006]For then, the purpose of forming the film which prevents an organic compound granular material dispersing out of an evaporation source, and does not have a pinhole during evaporation. "JP,6-349809, A In the evaporation source for organic compounds heats the evaporation material container which accommodated the organic compound raw material, and it was made to evaporate an organic compound, A filter is formed in the upper part of an organic compound evaporation source, and the evaporation source for organic compounds it was made not to disperse organic compound raw material powder out of an evaporation material container" is proposed. And the foam metal is used as a filter.

[0007]However, even if it can prevent scattering of organic compound raw material powder with a filter (foam metal) by said JP,6-349809,A in the case of the evaporation source for organic compounds of a proposal, the impurity of a raw material monomer will pass a filter (foam metal) with a raw material monomer. Therefore, if thickness is a thin film below 0.1 micrometer ( $1 \times 10^{3**}$ ), there is little influence, but if thickness forms the thick film more than 10 micrometer ( $1 \times 10^{5**}$ ), this impurity will carry out nuclear growth and unevenness of not less than several micrometers will be generated.

[0008]If an amount of evaporation is controlled and only the raw material monomer whose purity is 100% is evaporated using the difference of the maximum vapor tension of a raw material monomer, this problem is solvable, but membrane formation speed becomes 1/5 or less in this case, and it is not practical.

[0009]This invention solves the above conventional problems, and removes the impurity of a raw material monomer within an evaporation source, and an object of this invention is to provide the method for film deposition of the vacuum treatment chamber having the evaporation source and evaporation source which can form an organic compound film with little particle, and an organic compound film.

[0010]

[Means for Solving the Problem]In an evaporation source for an evaporation source of this invention to evaporate two kinds of raw material monomers of an organic compound film formed on a substrate in a vacuum, the feature of having considered at least one evaporation source as composition which attached a heating cooling system and the exhaust to an evaporation source among evaporation sources is carried out.

[0011]In a vacuum treatment chamber having an evaporation source for a vacuum treatment chamber having an evaporation source to evaporate two kinds of raw material monomers of an organic compound film formed on a substrate in a vacuum, the feature of having considered at least one evaporation source as composition which attached a heating cooling system and the exhaust to an evaporation source among evaporation sources is carried out.

[0012]In a method of a method for film deposition of an organic compound film evaporating [ method ] two kinds of raw material monomers of an organic compound film from each evaporation source in a vacuum treatment chamber, carrying out vapor deposition polymerization on a substrate, and forming an organic compound film, Evaporation of at least one raw material monomer is evaporated using an evaporation source which attached a heating cooling system and the exhaust in an evaporation source among raw material monomers.

[0013][OPERATION] A heating cooling system which heats a raw material monomer and with which while going into an evaporation source which attached a heating cooling system and the exhaust stands

in a row in an evaporation source is cooled, and by exhausting with the exhaust, using a difference of maximum vapor tension, sublimation refining is carried out and only a raw material monomer comes to adhere in a heating cooling system cooled. At this time, since it remains in the original evaporation source, an impurity in a raw material monomer can be separated easily.

[0014]Next, by stopping exhaust air of the exhaust, exhausting from the vacuum treatment chamber side connected to a heating cooling system, and stopping cooling of a heating cooling system and heating this, a raw material monomer which had adhered in this heating cooling system evaporates, and it is introduced in a vacuum treatment chamber. It vapor-deposits and polymerizes on a raw material monomer of another side where a raw material monomer was heated by other evaporation sources, it evaporated, and while it was introduced in a vacuum treatment chamber was introduced in a vacuum treatment chamber, and a substrate, and an organic compound film comes to be formed.

[0015]

[Embodiment of the Invention]The evaporation source of this invention is an evaporation source used as the mechanism provided with 2 stage structures with the evaporation source which attached the evacuation device which can exhaust uniquely the inside of an evaporation source, and a heating cooler style and an evaporation source for one evaporation source among the evaporation sources which evaporate a raw material monomer.

[0016]The composition of the evaporation source of this invention is explained based on an accompanying drawing.

[0017]Drawing 1 shows one example of the evaporation source of this invention.

[0018]Among the figure, one shows the whole evaporation source and has two-copy composition of the evaporation source 1a and the evaporation source 1b.

[0019]The evaporation source 1a comprises the evaporation source heater 5 which has covered the crucible 4 and the evaporation tub 2 of the product made from aluminum for being filled up with the evaporation tub 2, the raw material monomer 3, and the raw material monomer 3, or copper.

[0020]The evaporation source 1b comprises the vacuum housing heater 7 which has covered the metal vacuum housing 6 and the vacuum housing 6. And in the vacuum housing 6, the metal cylindrical cups 9 which circulate through water or a refrigerant like an antifreeze solution, and can be cooled via the refrigerant circulation machine 8 are arranged.

[0021]The evaporation source 1a and the evaporation source 1b are connected for the piping 11 which equips the evaporation source 1a side with the piping heater 11a via the valve 10, and the piping 12 which equips the evaporation source 1b side with the piping heater 12a.

[0022]The evaporation source 1b is connected with the vacuum pumping system which is not illustrated via the exhaust valve 13. The evaporation source 1b was connected with the monomer nozzle in the vacuum treatment chamber of an omnidirectional vapor-deposition-polymerization device (Japan vacuum-technology incorporated company make and trade name VEP3040) via the valve 14.

[0023]Thus, the evaporation source 1b is the composition provided with the heating cooling system which comprises the vacuum housing 6, the vacuum housing heater 7 which has covered the vacuum housing 6, and the cylindrical cup 9 provided with the cooler style in the vacuum housing 6, and the exhaust which comprises the vacuum pumping system connected via the exhaust valve 13.

[0024]Next, the composition of the vacuum treatment chamber having the evaporation source of said composition is explained based on an accompanying drawing.

[0025]Drawing 2 is a lineblock diagram of one example at the time of connecting the evaporation source

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(pyromellitic acid which is an impurity of PMDA) remained in the crucible 4 within the evaporation source 1a.

[0038]Then, closed the valve 10 and the valve 13, and cooling of the cylindrical cup 9 by a circulation \*\*\*\* refrigerant was stopped via the refrigerant circulation machine 8, and PMDA which has adhered to the cylindrical cup 9 with the vacuum housing heater 7 was heated in temperature of  $210 \pm 0.2$  °C.

[0039]Next, the crucible 19 within the evaporation source 1c was filled up with 200g of ODA as the raw material monomer 18. The valve 21 was opened and the pressure within the evaporation source 1c was beforehand set as  $1.3 \times 10^{-3}$  Pa ( $1 \times 10^{-5}$  Torr) via the vacuum pumping system linked to the exhaust valve 25 of the vacuum treatment chamber 15.

[0040]Then, the valve 21 was closed and ODA in the evaporation tub 19 was heated in temperature of  $183 \pm 0.2$  °C with the evaporation source heater 20.

[0041]The vacuum pumping system piping 27 was heated for the vacuum treatment chamber 15 in temperature of  $200 \pm 0.2$  °C with the piping heater 27a with the vacuum treatment chamber heater 26 again, respectively.

[0042]Next, opened the valve 14 and the valve 21 simultaneously, and PMDA was introduced in the vacuum treatment chamber 15 from the monomer nozzle 16 via the valve 14, and ODA was introduced in the vacuum treatment chamber 15 from the monomer nozzle 23 via the valve 21.

[0043]PMDA into the vacuum treatment chamber 15, 1 hour after introduction of ODA and the valve 14, and the valve 21 were closed simultaneously, PMDA into the vacuum treatment chamber 15 and introduction of ODA were suspended, and the polyimide film of 10 micrometers ( $1 \times 10^5$  Å) of thickness was formed on the whole substrate 24 surface.

[0044]Membrane formation speed of the polyimide film to the substrate 24 was considered as a part (min) for 16 micrometer ( $1.6 \times 10^6$  Å). It was made to evaporate PMDA and ODA in the mole ratio of 1:1 so that a polyimide film might be formed stoichiometrically. The temperature of the substrate 24 was  $200 \pm$  °C during membrane formation. The pressure in the vacuum treatment chamber 15 under membrane formation was 0.1 Pa ( $1 \times 10^{-3}$  Torr).

[0045]Then, after making the inside of the vacuum treatment chamber 15 into ordinary pressure, when the substrate 24 was taken out from the inside of the vacuum treatment chamber 15 and the substrate 24 was seen, the beautiful polyimide film with very little unevenness was formed in the surface.

[0046]The surface state [metallurgical microscope photograph (one 100 times the magnification of this)] of the polyimide film formed on the substrate 24 is shown in [drawing 3](#).

[0047]An one comparative example comparative example is an example of membrane formation of a polyimide film by a conventional method, using pyromellitic dianhydride (the following PMDA is called) and 4,4'-diaminodiphenyl ether (ODA is called below) as a raw material monomer of an organic compound film.

[0048]The plate-like thing with a 100 mm by [ size ] 100 mmx thickness [ made from stainless steel ] of 1 mm was used as the substrate 24.

[0049]This comparative example is a case where a polyimide film is formed without operating the evaporation source 1b shown in [drawing 2](#) like a conventional method. And the exhaust valve 13 was changed into the state where it always closed, and changed the valve 14 into the state where it always opened. The vacuum housing 6 of the evaporation source 1b was heated for the piping 12 in temperature of  $200 \pm 0.2$  °C with the vacuum housing heater 7 with the piping heater 12a again.

[0050]First, the crucible 4 within the evaporation source 1a was filled up with 200g of PMDA(s) as the

raw material monomer 3. And the exhaust valve 25 connected with the valve 10 in the vacuum treatment chamber 15 was opened, and the pressure within the evaporation source 1a was beforehand set as  $1.3 \times 10^{-3} \text{ Pa}$  ( $1 \times 10^{-5} \text{ Torr}$ ) via the vacuum pumping system linked to the exhaust valve 25.

[0051]Then, the valve 10 was closed and PMDA in the evaporation tub 2 was heated in temperature of  $210 \pm 0.2$  with the evaporation source heater 5. The piping 11 was heated in temperature of  $200 \pm 0.2$  with the piping heater 11a.

[0052]Next, the crucible 19 within the evaporation source 1c was filled up with 200g of ODA as the raw material monomer 18. The valve 21 was opened and the pressure within the evaporation source 1c was beforehand set as  $1.3 \times 10^{-3} \text{ Pa}$  ( $1 \times 10^{-5} \text{ Torr}$ ) via the vacuum pumping system linked to the exhaust valve 25 of the vacuum treatment chamber 15.

[0053]Then, the valve 21 was closed and ODA in the evaporation tub 19 was heated in temperature of  $183 \pm 0.2$  with the evaporation source heater 20. The piping 22 was heated in temperature of  $200 \pm 0.2$  with the piping heater 22a.

[0054]The vacuum pumping system piping 27 was heated for the vacuum treatment chamber 15 in temperature of  $200 \pm 0.2$  with the piping heater 27a with the vacuum treatment chamber heater 26 again, respectively.

[0055]Next, opened the valve 10 and the valve 21 simultaneously, and PMDA was introduced in the vacuum treatment chamber 15 from the monomer nozzle 16 via the valve 10, and ODA was introduced in the vacuum treatment chamber 15 from the monomer nozzle 23 via the valve 21.

[0056]PMDA into the vacuum treatment chamber 15, 1 hour after introduction of ODA and the valve 10, and the valve 21 were closed simultaneously, PMDA into the vacuum treatment chamber 15 and introduction of ODA were suspended, and the polyimide film of 10 micrometers ( $1 \times 10^{-5}$ ) of thickness was formed on the whole substrate 24 surface.

[0057]Membrane formation speed of the polyimide film to the substrate 24 was considered as a part (min) for 16 micrometer ( $1.6 \times 10^{-6}$ ). It was made to evaporate PMDA and ODA in the mole ratio of 1:1 so that a polyimide film might be formed stoichiometrically. The temperature of the substrate 24 was  $200 \pm$  during membrane formation. The pressure in the vacuum treatment chamber 15 under membrane formation was  $0.1 \text{ Pa}$  ( $1 \times 10^{-3} \text{ Torr}$ ).

[0058]Then, after making the inside of the vacuum treatment chamber 15 into ordinary pressure, when the substrate 24 was taken out from the inside of the vacuum treatment chamber 15 and the substrate 24 was seen, the irregular polyimide film was formed in the surface.

[0059]The surface state [metallurgical microscope photograph (one 100 times the magnification of this)] of the polyimide film formed on the substrate 24 is shown in [drawing 4](#).

[0060]As for the comparative example 1 by the conventional method which does not use the evaporation source of this invention, it turns out to Example 1 using the evaporation source of this invention having the even surface that the surface is unevenness so that clearly from [drawing 3](#) and [drawing 4](#).

[0061]Next, we decided to investigate the relation between the cooking temperature of PMDA at the time of changing various cooking temperature of PMDA and forming a polyimide film, and the particle density of the formed polyimide film.

[0062]the film formation condition of example 2 polyimide film -- \*\* board: -- slide glass (size [ of 76 mm x 26 mm ] x1 mm in thickness)

Cooking temperature ODA:  $183 \pm 0.2$  PMDA of a raw material monomer :  $210 \pm 0.2$  \*\*, two kind

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density on the temperature of a raw material monomer, it turns out that the comparative example 2 by the conventional method which does not use the evaporation source of this invention depends for particle density on the temperature of a raw material monomer, so that clearly from Table 1.

[0068]The composition of \*\*\*\*\* provided with the evaporation source of this invention is not limited to the composition shown in said drawing 2 (the one evaporation source 1 of drawing 1 is connected to the vacuum treatment chamber of an omnidirectional vapor-deposition-polymerization device [Japan vacuum-technology incorporated company make and trade name VEP3040]), and is good also as following composition. The composition is explained.

[0069]Drawing 5 is a lineblock diagram at the time of connecting the two evaporation sources 1 of drawing 1 to the vacuum treatment chamber of an omnidirectional vapor-deposition-polymerization device (Japan vacuum-technology incorporated company make and trade name VEP3040).

[0070]First, as shown in drawing 5, the evaporation source 1 (the evaporation source 1a and the evaporation source 1b) shown in drawing 1 was connected with the monomer nozzle 16 in the vacuum treatment chamber 15 via the valve 14.

[0071]To the device shown in drawing 5, it has the evaporation source 1a of this invention, the evaporation source 1a and the evaporation source 1b other than the evaporation source 1 which comprise the evaporation source 1b, the evaporation source 1c of the same composition, and 1 d of evaporation sources.

[0072]The evaporation source 1c comprises the evaporation source heater 20 which has covered the crucible 19 and the evaporation tub 17 of the product made from aluminum for being filled up with the evaporation tub 17, the raw material monomer 18, and the raw material monomer 18, or copper.

[0073]1 d of evaporation sources comprise the vacuum housing heater 29 which has covered the metal vacuum housing 28 and the vacuum housing 28. And in the vacuum housing 28, the metal cylindrical cups 31 which circulate through water or a refrigerant like an antifreeze solution, and can be cooled via the refrigerant circulation machine 30 are arranged.

[0074]And the evaporation source 1c and 1 d of evaporation sources are connected for the piping 33 which equips the evaporation source 1c side with the piping heater 33a via the valve 32, and the piping 34 which equips the evaporation source 1d side with the piping heater 34a.

[0075]1 d of evaporation sources are connected with the vacuum pumping system which is not illustrated via the exhaust valve 35. The evaporation source 1c and 1 d of evaporation sources were connected to the monomer nozzle 23 in the vacuum treatment chamber 15 via the valve 36.

[0076]Since other numerals are the same as that of drawing 2, explanation is omitted. The operation of the evaporation source 1c is the same as that of said evaporation source 1a, and the operation of 1 d of evaporation sources is the same as that of said evaporation source 1b.

[0077]Thus, the purity of both the raw material monomers of an organic compound film can be raised by having composition which attached the composition of the connection \*\*\*\*\* evaporation source to the vacuum treatment chamber, and all attached a heating cooling system and the exhaust to the evaporation source.

[0078]Of course, when using the vacuum treatment chamber having the evaporation source shown in drawing 5, it may be made to use 1 d of the evaporation sources 1a, the evaporation sources [ or ] 1b, the evaporation sources 1c, or evaporation sources.

[0079]Membrane formation of the organic compound film of this invention is not limited to said



polyimide film, evaporates a raw material monomer in sublimation, and also when producing a polymerization film (organic compound film), it can be used.

[0080]

[Effect of the Invention] Since the evaporation source of this invention considered at least one evaporation source as the composition which attached a heating cooling system and the exhaust to the evaporation source among evaporation sources, once vacuum refining of the raw material monomer is carried out to an evaporation source between heating cooling systems, it is effective in the ability to obtain easily the raw material monomer of an organic compound with higher purity. Since the raw material monomer of an organic compound film can be refined in a vacuum, a raw material monomer cannot react to the moisture in the atmosphere, and it can supply in the state where purity is high.

[0081] Since the vacuum treatment chamber having the evaporation source of this invention considered at least one evaporation source as the composition which attached a heating cooling system and the exhaust to the evaporation source among the evaporation sources linked to a vacuum treatment chamber, Once vacuum refining of the raw material monomer is carried out to an evaporation source between heating cooling systems, it has an effect which can supply easily the raw material monomer of an organic compound with higher purity in a vacuum treatment chamber. Since the raw material monomer of an organic compound film can be refined in a vacuum, a raw material monomer cannot react to the moisture in the atmosphere, and it can supply in a vacuum treatment chamber in the state where purity is high.

[0082] Since it was made for the method for film deposition of the organic compound film of this invention to evaporate evaporation of at least one raw material monomer among raw material monomers from the evaporation source which attached a heating cooling system and the exhaust to the evaporation source, Once vacuum refining of the raw material monomer is carried out to an evaporation source between heating cooling systems, it can evaporate an organic compound with higher purity as a raw material monomer, and. By using the raw material monomer of the refined organic compound, there is an effect which can form very few organic compound films of particle easily. Since the raw material monomer of an organic compound film can be refined in a vacuum, a raw material monomer cannot react to the moisture in the atmosphere, and vapor deposition polymerization can be carried out on a substrate in the state where purity is high.

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[Translation done.]